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14. ABSTRACT This report results from a contract tasking RWTH Aachen as follows: The aim of this project is to contribute towards the development of novel tribological materials. It will study a solid solution of this fascinating new class of nanolaminated materials using both theoretical and experimental means. The M2InC system was selected based on our recent EOARD project (FA8655-05-1-3009). Our specific research directions are 1) to tailor shearing in Sc2InC-Y2InC solid solution using ab initio calculations and 2) to synthesize Sc2InC-Y2InC thin films using magnetron sputtering and to determine the correlation between composition, structure, and mechanical properties thereof.					
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FINAL REPORT

Ab Initio Calculations and Synthesis of Sc_2InC – Y_2InC Solid Solution

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Our aim is to contribute towards the development of novel tribological materials. We propose to study a solid solution of this fascinating new class of nanolaminated materials using both theoretical and experimental means. The M_2InC system ($\text{M} = \text{Y}$ and Sc) was selected based on our recent EOARD project (FA8655-05-1-3009).

Our specific research directions are:

Goal 1: To tailor shearing in $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ solid solution using *ab initio* calculations (to be reached within 6 months).

Goal 2: To synthesize $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ thin films using magnetron sputtering and to determine the correlation between composition, structure, and mechanical properties thereof (to be reached within 12 months).

To reach these goals, the following tasks need to be accomplished, as outlined in Table 1:

Table 1: Time schedule

Task	1	2	3	4	5	6	7	8	9	10	11	12
1 Structure relaxation												
2 Bonding and shearing												
3 Synthesis and characterization												
Magnetron sputtering												
Energy dispersive x-ray analysis												
x-ray diffraction												
Nanoindentation												
Tribological analysis												

$\text{Y}_{2-x}\text{Sc}_x\text{InC}$ structures have been relaxed in terms of ionic positions as well as volumes via the lattice parameter a and the hexagonal c/a ratio. We have not explored spin polarization since it gave only minute energy corrections for Cr_2AlC ¹ and V_2AlC ². Figure 1 shows two configurations considered for $\text{Y}_{2-x}\text{Sc}_x\text{InC}$, termed A and B, when there are more structural arrangements of M elements possible (M metallic sublattice distribution). This allows for probing the configuration contribution to the total energy, but may also have relevance for the elastic properties. In addition, we

¹ J. M. Schneider, Z. Sun, R. Mertens, F. Uestel, and R. Ahuja, Solid State Commun. **130**, 445 (2004).

² J. M. Schneider, M. Mertnes, and D. Music, J. Appl. Phys. **99**, 013501 (2006).

have investigated the possibility of synthesis by calculating the energy of formation (E_f) as compared to elements. These results are given in Table II.

Table II: Structural data, energy of formation, and elastic constants.

x	a (Å)	c/a	V (Å ³ /atom)	B (GPa)	C_{44} (GPa)	E_f (eV/atom)
0.00	3.514	5.033	23.636	74	43	-0.364
0.25	3.543	4.795	23.090	76	48	-0.404
0.50(A)	3.522	4.711	22.272	79	56	-0.425
0.50(B)	3.522	4.714	22.290	79	51	-0.424
0.75(A)	3.498	4.663	21.612	81	57	-0.441
0.75(B)	3.499	4.662	21.627	81	55	-0.441
1.00(A)	3.475	4.623	21.006	84	56	-0.458
1.00(B)	3.480	4.611	21.044	84	59	-0.460
1.25(A)	3.453	4.586	20.435	87	59	-0.478
1.25(B)	3.456	4.578	20.452	86	57	-0.479
1.50(A)	3.429	4.556	19.886	90	63	-0.502
1.50(B)	3.430	4.554	19.896	90	59	-0.502
1.75	3.405	4.526	19.340	93	62	-0.529
2.00	3.272	5.028	19.056	93	56	-0.517

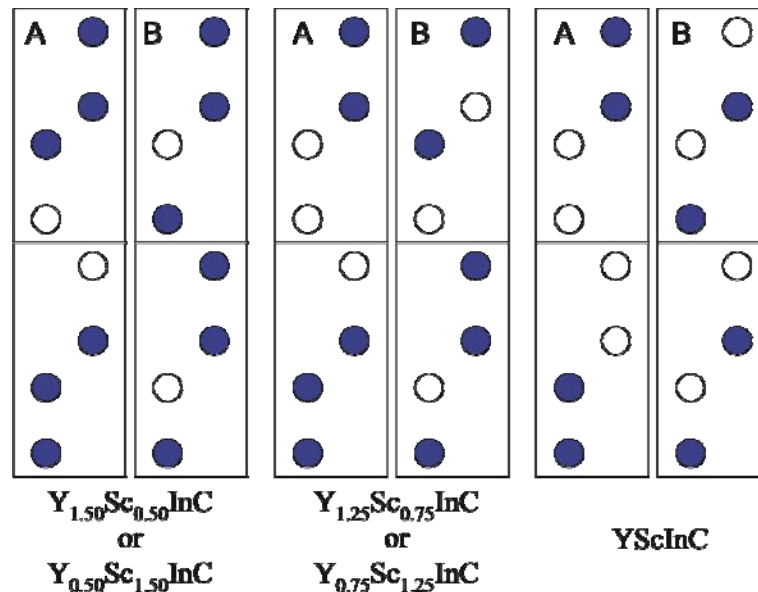


Figure 1 Considered configurations of Sc_2InC – Y_2InC solid solution. Open and solid spheres represent M elements (Sc or Y).

The calculated values of equilibrium volume as a function of the solution content x are shown in Fig. 2. There are no significant differences in the equilibrium volume with respect to the M metallic sublattice distribution. As Y is replaced with Sc, the equilibrium volume decreases by 19.4% from 23.636 to 19.056 Å³/atom. A small negative deviation from the mechanical mixture (the so-called Vegard's rule), depicted with a dashed line, can be observed. This deviation may be understood based

on alterations in bond angles and consequently lattice parameters, as discussed in a previous work on $\text{Nb}_{2-x}\text{W}_x\text{AlC}$ ¹.

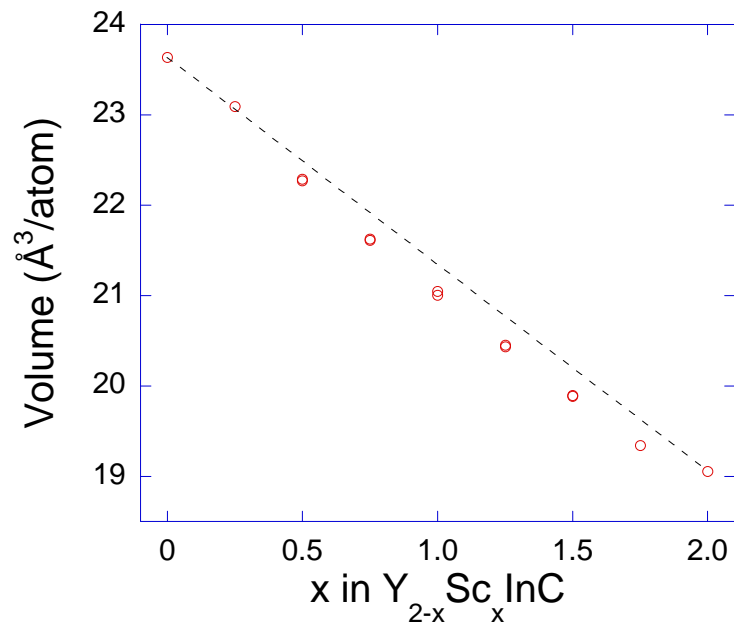


Figure 2 Volume of $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ as a function of the solution content x .

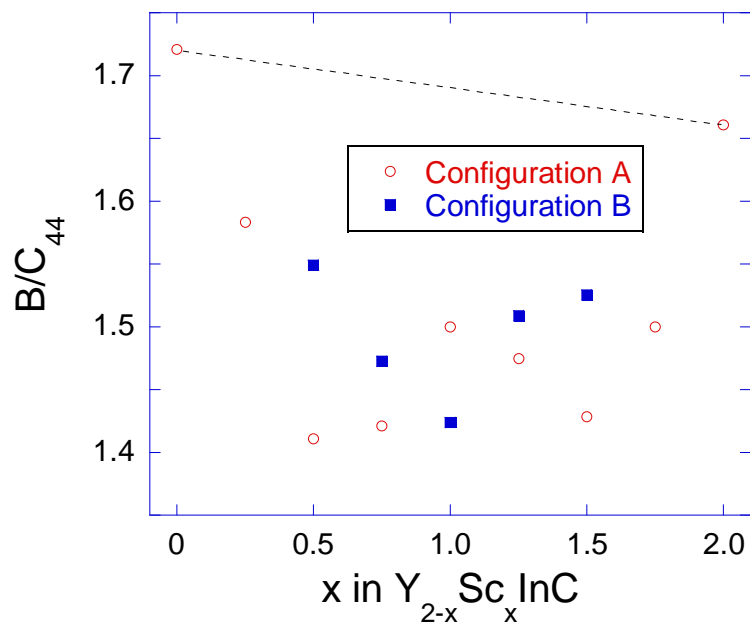


Figure 3 Bulk modulus (B) to C_{44} ratio for $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ as a function of the solution content x .

In Fig. 3 the calculated bulk modulus to C_{44} ratios are shown as a function of solution content x . As x is increased from 0 to 2, the bulk modulus increases by 25.7% from 74 to 93 GPa. The general trend for C_{44} data is that its value also increases in the x -range probed, but the functional dependence is more complex, it depends on both x and the M metallic sublattice distribution (see Table II). Hence, the bulk modulus to C_{44} ratios

¹ J. M. Schneider, Z. Sun, and D. Music, J. Phys.: Condens. Matter **17**, 6047 (2005).

are in the range from 1.4 to 1.7, which is a striking range covered. It may be envisioned that due to controlled changes in synthesis parameters, such as ion energy, ion flux, substrate temperature, and plasma density, the M metallic sublattice distribution can be affected or even tailored. This may in turn allow for tailoring of shear properties. This behavior of the elastic properties may be understood studying changes in the chemical bonding. The effect of the substitution can be seen in Fig. 4, where charge density distributions for $\text{Y}_{1.75}\text{Sc}_{0.25}\text{InC}$, YScInC (configurations A and B), and $\text{Y}_{0.25}\text{Sc}_{1.75}\text{InC}$ are given. Analyzing the M-C bonding, it can be concluded that the bonding is characterized by covalent and ionic contributions. The coupling between the MC layer and the In layer is weak in both compounds. This is consistent with our previous work^{1,2}. Based on the Harrison's rule³, the Sc-C bond is by a factor 1.76 stronger than the Y-C bond. Furthermore, it can be observed in Fig. 4 that the strength of the M-In bond (MC and In coupling) increases with an increase in x . Thus, by replacing Y with Sc, an increase in the bulk modulus is expected. In a previous work⁴, we have found that the shearing behavior of MAX phases may be correlated to the filling of shear resistant d bands in the vicinity of the Fermi level (dd interaction or MC-MC coupling). As there is no change in the valence electron concentration as x increases, the Fermi energy may be directly correlated to the filling of shear resistant bands. In Fig. 5, C_{44} data as a function of the Fermi energy for $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ are given. It is apparent that the filling of the shear resistant bands can be related to the C_{44} values and hence it is possible to explain the bulk modulus to C_{44} ratios obtained.

To study the relative phase stabilities, we have calculated the energy of formation versus x . Figure 6 shows the energy of formation for $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ as a function of the solution content x . There are no significant differences in the energy of formation with respect to the M metallic sublattice distribution. The energy of formation differences of all quaternary compounds to the mechanical mixture is negative, indicating a stable solid solution. At temperatures above 0 K, the stability depends on the Gibbs free energy and hence a contribution of enthalpy and entropy. We base our stability discussion on calculated enthalpy differences at 0 K. The contributions of entropy as well as the temperature dependence of the enthalpy have to be included in the discussion in order to determine the actual phase stabilities at temperature above 0 K. However, our previous calculations⁵ of the solubility within $(\text{M}_x\text{M}'_{2-x})\text{AlC}$, where M and $\text{M}' = \text{Ti}, \text{V}, \text{and Cr}$, was consistent with the published experimental solubility data⁶. The magnitude of the energy of formation difference of previously investigated systems to the mechanical mixture thereof is comparable to the corresponding difference for the $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ solid solution studied here. Hence, it is likely that this solid solution can be formed by sputtering. At present, we are growing these structures and the results will be presented in the next report.

¹ D. Music, Z. Sun, R. Ahuja, and J. M. Schneider, Phys. Rev. B **73**, 134117 (2006).

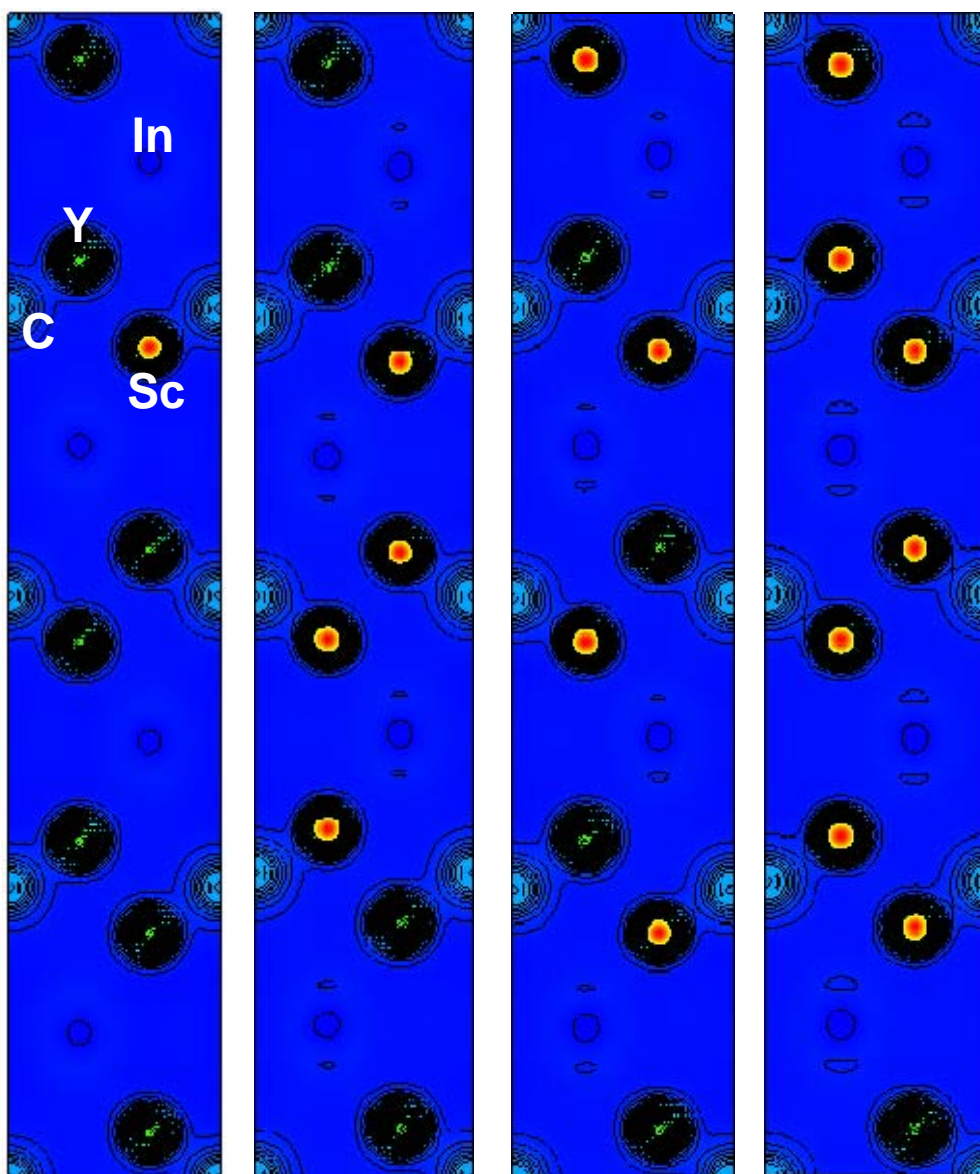
² D. Music, Z. Sun, and J. M. Schneider, Solid State Commun. **133**, 381 (2005).

³ D.-Y. Cho, J.-Y. Kim, B.-G. Park, K.-J. Rho, J.-H. Park, H.-J. Noh, B. J. Kim, S.-J. Oh, H.-M. Park, J.-S. Ahn, H. Ishibashi, S.-W. Cheong, J. H. Lee, P. Murugavel, T. W. Noh, A. Tanaka, and T. Jo, Phys. Rev. Lett. **98**, 217601 (2007).

⁴ D. Music, Z. Sun, A. A. Voevodin, and J. M. Schneider, Solid State Commun. **139**, 139 (2006).

⁵ Z. Sun, R. Ahuja, and J. M. Schneider, Phys. Rev. B **68**, 224112 (2003).

⁶ J. C. Schuster, H. Nowotny, and C. Vaccaro, J. Solid State Chem. **32**, 213 (1980).



Y_{1.75}Sc_{0.25}InC YScInC(A) YScInC(B) Y_{0.25}Sc_{1.75}InC

Figure 4 Electron density distributions in the $(11\bar{2}0)$ plane for several $Y_{2-x}Sc_xInC$ configurations. The electron density increases from 0.1 (dark blue) to 9.8 (dark red) electrons/Å³.

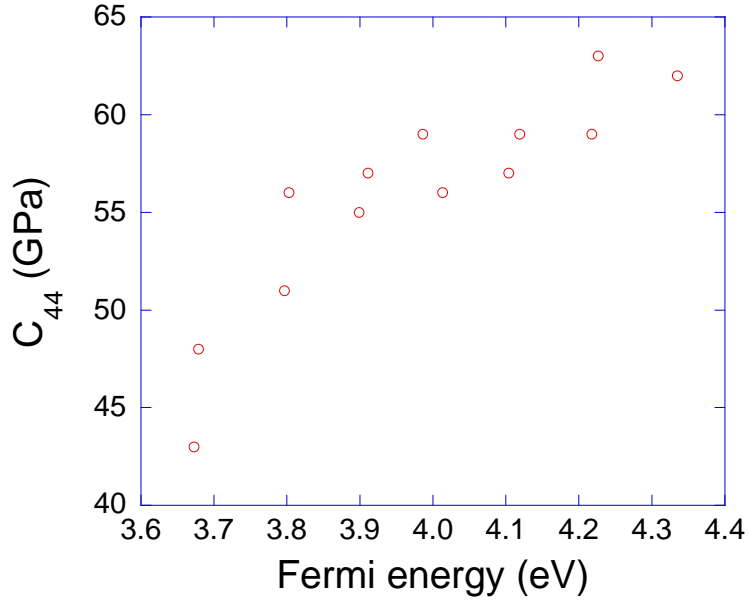


Figure 5 C_{44} versus Fermi energy for $Y_{2-x}Sc_xInC$.

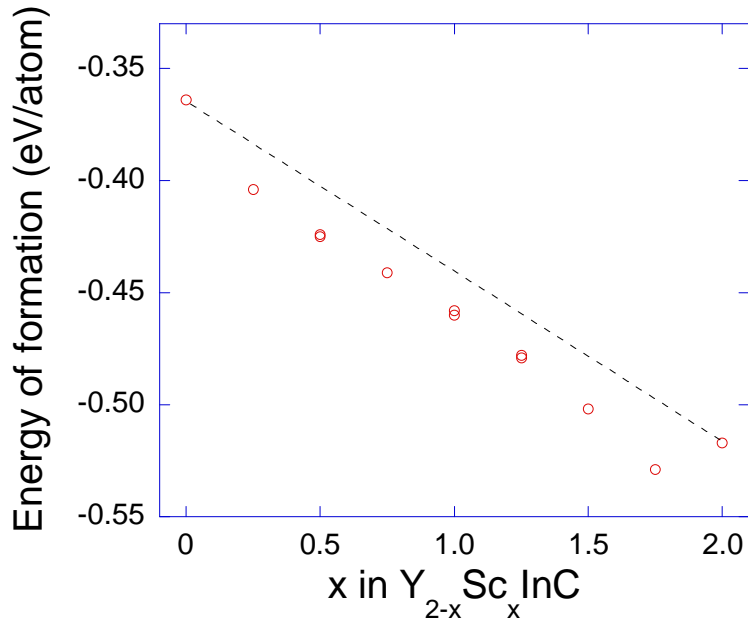


Figure 6 Energy of formation for $Y_{2-x}Sc_xInC$ as a function of the solution content x .

Our experimental task was to synthesize $Y_{2-x}Sc_xInC$ thin films using magnetron sputtering. This was attempted using a home-build combinatorial sputter deposition platform. The thin film growth experiment was started with the investigation of the Y-In binary system. A compositionally spread Y-In thin film was prepared by co-sputtering of elemental Y and In targets. The deposition was made on a 2 inch Si(100) substrate without intentional heating. After several depositions, the quality of as-deposited Y-In films appeared not to be sufficient enough for the further investigation of the $Y_{2-x}Sc_xInC$ solid solutions. The delamination and oxidation of the films were commonly observation. However, the microstructural investigation of the as-

deposited films revealed an interesting phenomenon, namely the formation of In fibers on the films, as shown in Fig. 7. The thickness of the fibers ranges from a few hundred nanometers to a few micrometers. It is found that the In fibers are formed spontaneously upon exposure of the films to air. Thus, we did not form the $Y_{2-x}Sc_xInC$ solid solutions.

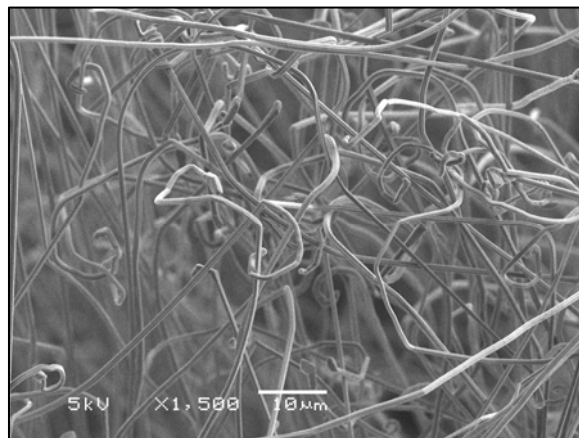


Figure 7 Scanning electron micrograph of In fibers.

Since we did not form $Y_{2-x}Sc_xInC$ thin films, we could not have carried out tribological studies of MAX phases with our partners at AFRL/MLBT, as originally planned. Therefore, we are currently growing Cr_2AlC and Ti_2AlC thin films on M50 steel and Inconel 718 substrates for tribological testing at AFRL/MLBT. Furthermore, we have also studied a possibility to synthesize MAX phases in the Ti-Al-C system at lower substrate temperatures, which may be central for many applications, including wear resistance.

A major challenge in processing the nanolaminates is a reduced synthesis temperature. For instance, Ti_3AlC_2 can be grown at 1400 – 1600 °C by hot isostatic pressing¹ or by solid-liquid reaction synthesis and simultaneous *in-situ* hot pressing process². Riley and Kisi have demonstrated that Ti_3AlC_2 can be synthesised by the rapid intercalation of Al in $TiC_{0.67}$ (space group $Fm\bar{3}m$) at 400 – 600 °C below the conventional processing temperature³. The authors have suggested that, after the ingress of molten Al into $TiC_{0.67}$, vacancy ordering facilitates the formation of Ti_3AlC_2 . Density functional theory was used to evaluate the energetics of point defects in TiC_x ($x < 1$): C vacancies and Al substitution at a C site. Our ambition is to contribute towards understanding the underlying atomic mechanisms enabling the Al intercalation into TiC_x and the subsequent formation of Ti_3AlC_2 . The difference between the energy of formation for an Al substitution at a C site and a bulk C vacancy is 0.224 eV (Fig. 8 shows the deformation of the TiC_x lattice upon introduction of a C vacancy). Furthermore, only 49 meV/vacancy is required to order the existing bulk C vacancies. Surface effects were also considered: the energy of formation for Al on $TiC(100)$ at a vacant surface C site is smaller by 2.779 eV than in

¹ N. V. Tzenov and M. W. Barsoum, J. Am. Ceram. Soc. **83**, 825 (2000).

² X. H. Wang and Y. C. Zhou, Acta Mater. **50**, 3141 (2002).

³ D. P. Riley and E. H. Kisi, J. Am. Ceram. Soc. **90**, 2231 (2007).

the case of the C surface vacancy, indicating that Al is likely to be incorporated. Based on these energy differences, it is reasonable to assume that Ti_3AlC_2 is formed by Al surface ingress into TiC_x and that vacancy ordering takes place.

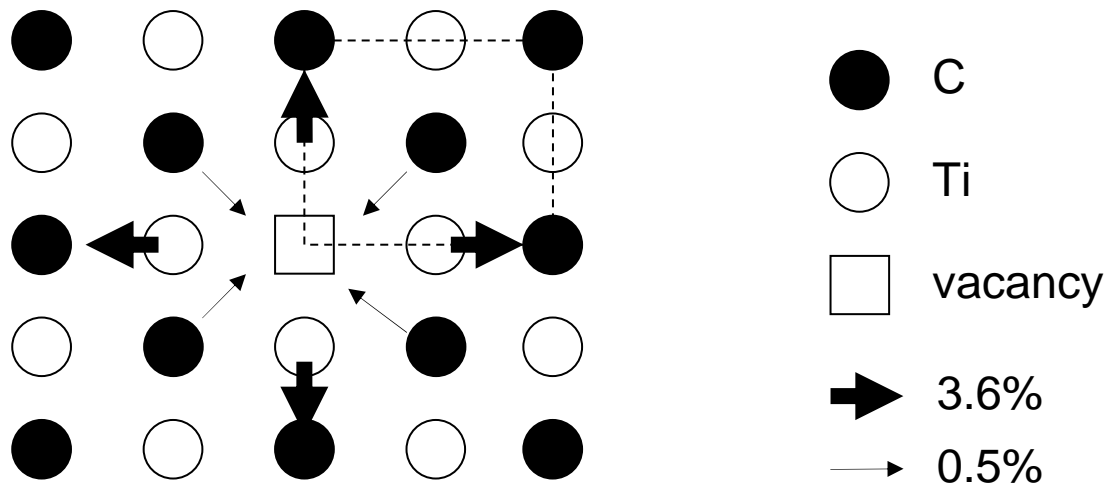


Figure 8 Local lattice relaxations, as indicated by arrows, in bulk TiC_x induced by the presence of a C vacancy. The (100) plane of the TiC supercell is shown.

In summary, $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ structures have been relaxed by means of *ab initio* calculations and analyzed in terms of chemical bonding and elastic properties. We find that $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ solid solutions are stable and prone to shearing due to weak coupling between MC and In nanolaminates, and hence show potential for application as solid lubricant. The bulk modulus to C_{44} ratios are in the range from 1.4 to 1.7, which is a striking range covered. Hence, our first goal of this project has been reached. Considering our second goal, we have attempted to grow $\text{Y}_{2-x}\text{Sc}_x\text{InC}$ thin films, but due to oxidation and delamination, we did not manage to reach the second goal. However, the microstructural investigation of the as-deposited Y-In films revealed an interesting phenomenon, namely, the formation of In fibers on the films. It is found that the In fibers are formed spontaneously upon exposure of the films to air. Currently, we are growing Cr_2AlC and Ti_2AlC thin films for tribological testing at AFRL/MLBT. Furthermore, we have also studied a possibility to synthesize MAX phases in the Ti-Al-C system at lower substrate temperatures, which may be central for many applications, including wear resistance.